

RANK DEPENDENCE OF ASSOCIATIVE EQUILIBRIA OF COAL MOLECULES IN SOLVENTS

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Keywords: associative equilibrium; extraction rate; intermolecular interaction

Introduction

Solvent-induced association (a conformational change) of several high-volatile bituminous coals was observed in hot toluene, hot chlorobenzene, and cold pyridine.^{1,2} It was proposed that the solvent-induced conformational change is due to two concerted processes: breaking secondary interactions originally present and forming new secondary interactions in a lower free energy state. This implies that associative equilibria between coal molecules will exist in solvents. In this paper, the rank dependence of the associative equilibria and intermolecular interactions is investigated.

Experimental Section

All ACS and HPLC grade chemicals were used without further purification. The coal samples were obtained from Exxon Research and Engineering Co., and the Pennsylvania State University Coal Bank. Their elemental analyses were reported in the previous paper.¹ Coal samples were ground and sifted under a nitrogen atmosphere. Minus 60 mesh particles were used in the experiments.

Approximately 2 to 5 g of each coal sample were placed in a 250 mL flask in 100 mL of pyridine and either stirred at room temperature or refluxed (115°C) under dry N₂ in an oil bath. One series of cooled samples was dried using a rotary evaporator, mixed with methanol, filtered, and rinsed with methanol several times. The coal was then dried to constant weight in the vacuum oven at 50°C. Another series of samples was filtered and the wet residues promptly Soxhlet-extracted.

The Diels-Alder reaction has been reported.¹ Maleic anhydride adducts formed using phenol solvent were precipitated in methanol, filtered, and then Soxhlet-extracted with methanol for 24 hrs. in order to eliminate by-products formed by reactions of maleic anhydride and phenol before removal of non-reacted maleic anhydride by Soxhlet extraction with H₂O. The by-products were easily extracted with methanol, which was verified by using a blank experiment without coal. The major molecular masses of by-products from coal, and those obtained using the blank experiment, were the same: 270, 322, and 362. Infrared spectra and X-ray diffraction studies were carried out as previously described.²

Results and Discussion

Pyridine extractability rectilinearly increases up to ca. 87 wt% C coal (named here as A-region), then decreases sharply with rank (87-90 wt% C: B-region).³ At still higher rank (>90 wt% C: C-region), only a few percent is extracted.

Pyridine extraction rate was compared for each region coal, and selected results are shown in Figure 1. A-region coal was promptly extracted within one or two days, while more than seven days were required for the extraction of B-region coal to be completed under the same conditions. C-region coal yields extract slowly, and the ultimate extractability is very small.

Pyridine extractability of the A-region coal was greater at the boiling point (115°C) than at room temperature,¹ but extraction yields of the A-region coal at 115°C and at 180°C were similar.^{3,4} However, pyridine extractability of the B-region coal at 180°C is much greater than that at 115°C.⁴

Since it was first reported by Harger and Illingworth^{5,6} that coals preheated at 200 to 400°C in an inert atmosphere give much higher yields of extract than unheated coals, the preheating effect has been investigated by several groups, and recently reviewed.⁷ Solvent extractability increases with preheating temperature, reaches a maximum, and then declines.^{3,8} However, the pyridine and chloroform extraction yields of the A-region coal were only slightly increased by preheating to 300°C, while the B-region coal was much more extractable after preheating at temperatures below 300°C.³ The dependence of the preheating effect on coal rank was recently studied by preheating at 250°C for 24 hrs.⁷ The effect was highly rank-dependent. Tetrahydrofuran extraction yields of higher-rank coals increased after preheating, while those of lower-rank coals decreased. These data show that A and B-region coals differ in their response to heating.

Heating the A-region coal at 115°C in chlorobenzene for seven days caused a decrease in pyridine extractability.¹ The same solvent treatment was given to a B-region coal, PSOC-1300 (89.9% C), in this study, but the pyridine extraction yield (24 hrs) of this treated coal increased to 18 wt% from 7 wt%. Figure 2 shows the change in pyridine extraction yields caused by soaking coal in pyridine at the boiling point for seven days for various A- and B-region coals. The pyridine extractabilities of coals dried after soaking in pyridine at room temperature for one day are also included in this figure. Pyridine extractabilities of the B-region coals significantly increased after soaking in pyridine at the boiling point for seven days contrary to those of the A-region coals. Pyridine extractabilities of the coals dried after soaking in pyridine at room temperature decreased for the A-region coals, but slightly increased for the B-region coals. These data show that the pyridine extractabilities of the A- and B-region coals after treatment with pyridine and chlorobenzene result in opposites.

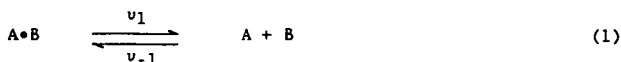
Aggregations are seen in phase separation phenomena such as precipitation, gelation, and crystallization. Dormans and van Krevelen³ studied precipitation from a pyridine soluble Soxhlet-extract at room temperature. Pyridine extracts from the A-region coal did not form precipitates after 240 hrs, while those from the B- and C-region coals yielded precipitates amounting to between 10 and 30 wt% of the extract. In the present study, the pyridine extract of an A-region coal, PSOC-1336 (84.1% C), was concentrated, filtered, and held at room temperature under nitrogen. The extract with concentration of 13.4 mg/cm³ showed no precipitate after 14 days, while the extract with concentration of 55.3 mg/cm³ precipitated 0.5 wt% of the extract after 5 days. The precipitate could be easily seen at the bottom of a flask. Concentrated pyridine extracts of other A-region coals, Illinois No. 6 (79.9% C) and Pittsburgh No. 8 (83.8% C), also formed precipitates if their concentration were more than 100 mg/cm³. van Krevelen's work suggests that high temperature (Soxhlet extraction) extracts of the B- and

C-region coals easily associate at low (room) temperature. The present work shows that high temperature extracts of the A-region coal do not associate at low temperature when diluted, but concentrated extracts do tend to associate.

All of the above data are summarized in Table I. These data can be understood as the result of change of the equilibrium state of coal molecules in solvents. The associative equilibria seem to be highly rank-dependent.

From the above results, it is suggested that extractability may be controlled by the equilibrium state between a solvent and coal. This is amendable to a quantitative treatment.

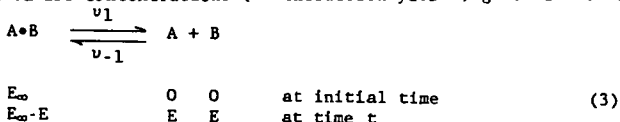
Assume that a complex A·B equilibrates with each component A and B in a solvent.



If the complex A·B is not extractable, components A and B are extractable with a solvent, and the rate v_1 is much greater than the rate v_{-1} , the extraction rate of each component is given as

$$\frac{dE}{dt} = k_1 (E_{\infty} - E) \quad (v_1 \gg v_{-1}) \quad (2)$$

where E and E_{∞} are concentrations (or extraction yields) given as follows



Therefore, an extraction yield at given time is

$$E = E_{\infty} (1 - e^{-k_1 t}) \quad (4)$$

where E_{∞} and k_1 are regarded as an ultimate extraction yield and an extraction rate constant, respectively. A similar equation was derived by Oele *et al.*⁹ for the extractive disintegration of bituminous coals at high temperatures (150 to 350°C) in an anthracene oil and β -naphthol. They assumed a zero order process for a forward disintegration at the initial step and additionally a first order process for a backward integration when extraction proceeds. Equation (4) is a first order rate. The rate constant k_1 is determined by extraction yields E_1 and E_2 at two different times t_1 and t_2 ,

$$k_1 = \frac{\ln \frac{E_{\infty} - E_1}{E_{\infty} - E_2}}{t_2 - t_1} \quad (5)$$

or by measurement of increment of extraction by half (τ)

$$k_1 = \frac{\ln 2}{\tau} \quad (6)$$

Calculated values using Equation (4) are shown in Figure 1 as well as experimental results for extractability versus extraction time. Extraction rate can be approximated by using Equation (4). Therefore, the dissociation of the coal-coal interactions can be thought of the major rate determining step in an extraction process. The slow rate of Soxhlet extraction is attributed to the slow dissociation (small k_1) of aggregated clusters. The stronger the physical interactions are, the smaller will be the rate constants k_1 . The poorer solvents are for the extract, the smaller rate constants k_1 will be. In the case of very small rate constants, high temperature could be required to overcome the activation energy to allow dissociation of components.

Since high temperatures and good solvents are apparently needed to dissociate the aggregated clusters in the B- and C-region coals (Table I), chemical reactivity for these coals should be promoted at the higher temperatures and good solvents which lead to dissociation, while that for the A-region coal should not be enhanced even at the same condition. The Diels-Alder reaction has been utilized to weaken the interaction between polynuclear aromatics in coals.^{1,10} In this work, maleic anhydride was reacted with each region coal in phenol at 115 and 180°C, and the product was pyridine-extracted.^{1,10} Increased extractability at 180°C was observed for all coals, but the increases for B- and C-region coals were much greater than that of the A-region coal. A-region extractability increased by 1/3, while the B- and C-region extractabilities increased by factors of 7 and 15, respectively. The enhancements of pyridine extractabilities for the B- and C-regions coals were particularly remarkable as compared with the results obtained by using a chlorobenzene solvent (115°C).

The IR absorptions between 1700 and 1750 cm^{-1} assigned to carbonyl vibrations in maleic anhydride adducts are shown in Figure 3 for a starting C-region coal, PSOC-688 (92.0% C), and its maleic anhydride adducts reacted under various conditions. These results demonstrate more maleic anhydride incorporation at higher temperature, although the Diels-Alder reaction is reversible and low temperatures are preferred for adduct formation. Pyridine is a good solvent but cannot be used for this reaction, because this solvent catalyzes the polymerization of maleic anhydride.¹⁰ These results suggest that the intermolecular interaction dissociable at high temperature play an important structural role in the B- and C-region coals and is responsible for the differences in behaviors shown in Table I for each region coal.

Figure 4 shows the change in the X-ray diffraction [002] band caused by reaction with maleic anhydride. This band is due to the parallel stacking of aromatic systems.¹¹ The magnitude and half-width of the maleic anhydride adduct of the PSOC-688 reacted in chlorobenzene at 115°C was identical with that of starting coal. The parallel stacking was obviously reduced after the maleic anhydride reaction in phenol at 180°C. This result implies that the incorporation of maleic anhydride decreases the number of face-to-face aromatic stacks, and that the face-to-face interaction may be responsible, in part, for the association in high-rank coal.

References

1. Nishioka, M.; Larsen, J. W. Energy & Fuels in press.
2. Nishioka, M.; Larsen, J. W. Prepr. Am. Chem. Soc. Div. Fuel Chem. 1990.
3. Dormans, H. N. M.; van Krevelen, D. W. Fuel 1960, 39, 273-292.
4. Illingworth, S. R. Fuel 1922, 24, 213-219.
5. Harger, J. J. Soc. Chem. Ind. 1914, 33, 389-392.
6. Illingworth, S. R. J. Soc. Chem. Ind. 1920, 39, 111-118.
7. Nishioka, M.; Larsen, J. W. Energy & Fuels 1988, 2, 351-355.
8. Wynne-Jones, W. F. K.; Blayden, H. E.; Shaw, F. Brennstoff-Chem. 1952, 33, 201-206.
9. Oele, A. P.; Waterman, H. I.; Goedkoop, M. L.; van Krevelen, D. W. Fuel 1951, 30, 169-178.
10. Quinga, E. M. Y.; Larsen, J. W. Energy & Fuels 1987, 1, 300-304.
11. Hirsh, P. B. Proc. Royal Soc. (London) 1954, A226, 143-169.

Table I. Differences in Behaviors in Extraction, Soaking, and Sitting Extract for Each Region Coal.

%C (daf)	A <87	B 87-90	C ^a >90
1. Pyridine extraction rate	fast	slow	
2. Temperature (115°C & 180°C) effect on pyridine extraction	small	large	
3. Preheating (200-400°C) effect on pyridine extraction	small	large	
4. Immersion in pyridine and removal of the solvent before pyridine extraction	decrease in extractability	increase in extractability	
5. Soaking in hot toluene or chlorobenzene before pyridine extraction	decrease in extractability	increase in extractability	
6. Precipitation of Soxhlet pyridine extracts at room temperature	no precipitation ^b	precipitation	

^aDifferences are very small because of very small ultimate extractability.

^bPrecipitation occurs only at high concentration.

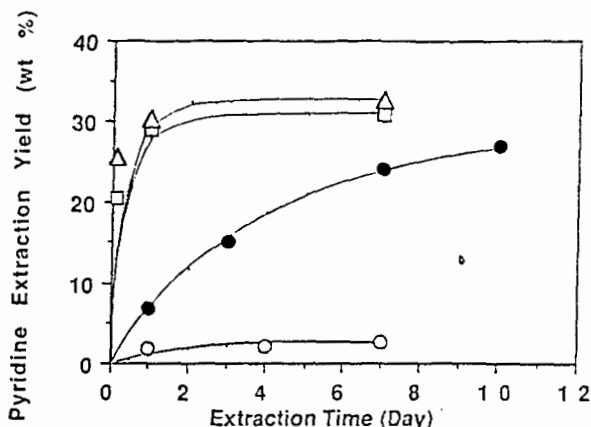


Figure 1. Pyridine extractability versus extraction time. Key: (\square) Illinois No. 6 (79.9% C) ($E_{\infty} = 31.2$, $k_1 = 2.3$), (Δ) PSOC-1336 (84.1% C) ($E_{\infty} = 32.8$, $k_1 = 2.3$), (\bullet) PSOC-1300 (89.9% C) ($E_{\infty} = 29.0$, $k_1 = 0.26$), and (\circ) PSOC-688 (92.0% C) ($E_{\infty} = 2.7$, $k_1 = 0.43$).

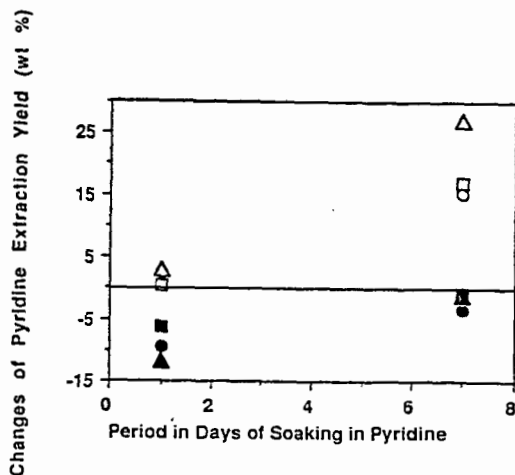


Figure 2. Changes of pyridine extractabilities of the A and B-region coals immersed in pyridine at the boiling point for seven days and their dried coals after immersing in pyridine at room temperature for one day. Key: (Δ) PSOC-991 (89.4% C), (\square) PSOC-1300 (89.9% C), (\circ) PSOC-721 (88.5% C), (\blacksquare) Illinois No. 6 (79.9% C), (\bullet) PSOC-1336 (84.1% C), and (\blacktriangle) Pittsburgh No. 8 (83.8% C).

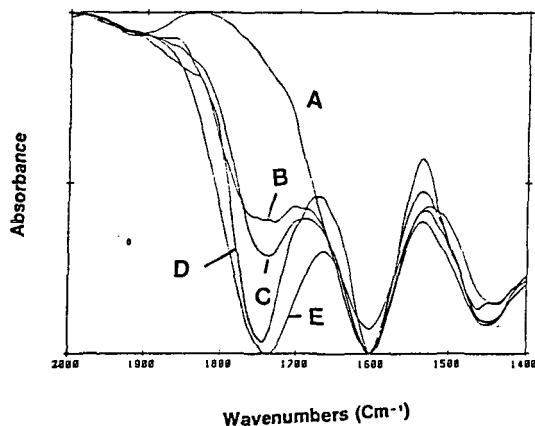


Figure 3. Overlay photoacoustic infrared Fourier transform spectra assigned to the carbonyl groups of (A) starting coal and maleic anhydride adducts of PSOC-688 reacted under selected solvents and temperature. Conditions of Diels-Alder reaction: (B) in chlorobenzene at 115°C, (C) in phenol at 115°C, (D) in phenol at 180°C, and (E) in 1,2-dichlorobenzene at 180°C.

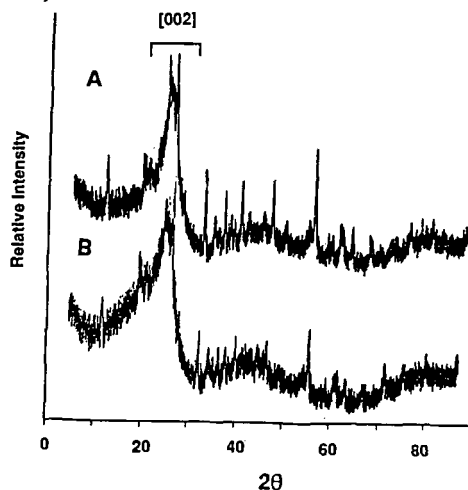


Figure 4. X-ray diffraction patterns of [002] band of maleic anhydride adducts of PSOC-688 reacted (A) in chlorobenzene at 115°C and (B) in phenol at 180°C.